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AMINO DERIVATIVES OF AROMATIC SULPHONES

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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DEGREE OF Bachelor of Science in Chemical Engineering

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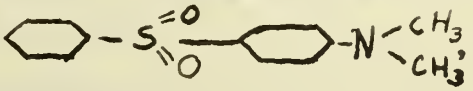
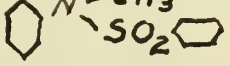
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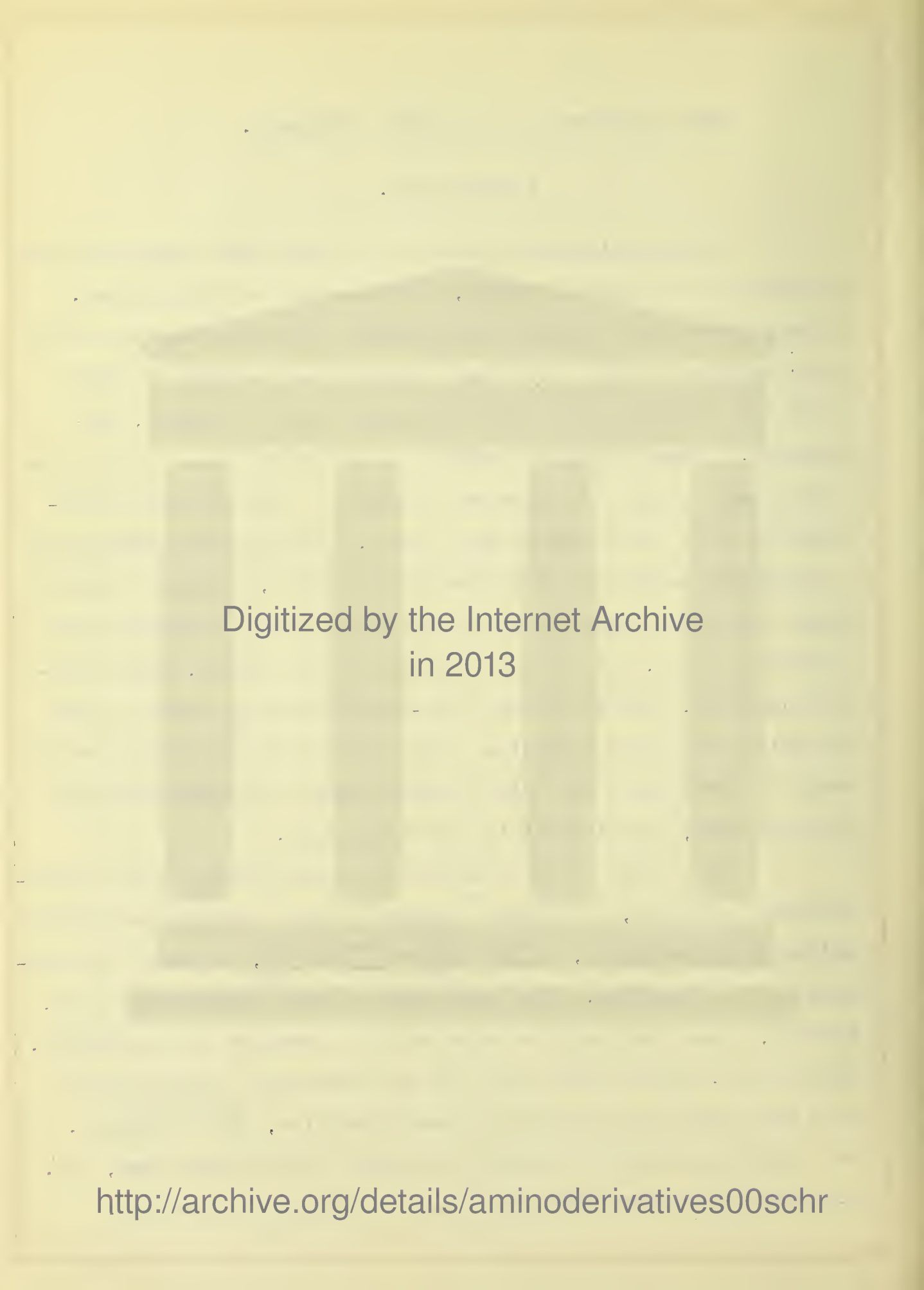
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AMINO DERIVATIVES OF AROMATIC SULPHONES.

Introduction.

Benzenesulphonyl chloride is an important reagent for the differentiation between primary, secondary and tertiary amines[1]. Primary amines form benzene sulphonamides which are soluble in alkali; secondary amines yield acyl derivatives insoluble in both acids and alkalies; while tertiary amines are, in general, non-reactive. Accordingly the method may be applied also for the separation and analysis of mixtures of amines. The procedure possesses at least two disadvantages: first, primary amines often yield considerable amounts of disulphonyl derivatives, compounds which in their solubility behavior agree with the sulphonyl derivatives of secondary amines, and second, certain tertiary amines, notably dimethylaniline, undergo unusual side-reactions which result in the formation of colored products. The present work was undertaken in order to investigate the latter reaction and is a continuation of previous work[2], carried out in this laboratory.

In a study of the reaction of dimethylaniline and benzenesulphonyl chloride, W. Michler[3] claimed to have isolated p-dimethylamino diphenylsulphone, , as one of the products of the reaction. The properties of this compound were not, however, those that would be expected of a compound of this nature. Moreover Dr. Oliver Kamm found that its properties agreed fairly well with those of benzenesulphonemethylanilide, . It was therefore thought advisable to prepare the true sulphone, i.e. p-dimethylaminodiphenylsulphone, and to study its properties.


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Historical Part.

R. Gnehm[4] in a paper published in 1877, mentions the fact that Michler prepared p-dimethylaminodiphenylsulphone by the interaction of benzenesulphonyl chloride and dimethylaniline. H. Hassencamp,[5] however, in a paper published in 1879 on the same reaction, does not mention anything about having detected such a compound.

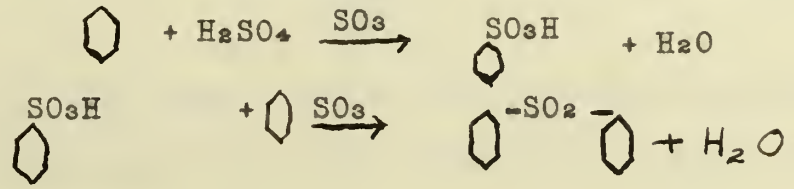
W. Michler and K. Meyer[3] in a paper published in 1879 describe the method followed in preparing the compound which they thought was p-dimethylaminodiphenylsulphone. Two moles of dimethylaniline were heated, one mole of benzenesulphonyl chloride was added in small portions, and the whole then heated for a short time. This was then supersaturated with ammonia and the dimethylaniline removed by steam distillation. The remainder was treated with hydrochloric acid, and the residue which was insoluble in the acid was recrystallized several times from alcohol. This was the compound which they thought was the true sulphone.

N. W. Wroby[2] in 1918, proved, however, that the compound that Michler and Meyer obtained was, in reality, benzenesulphonemethylanilide.

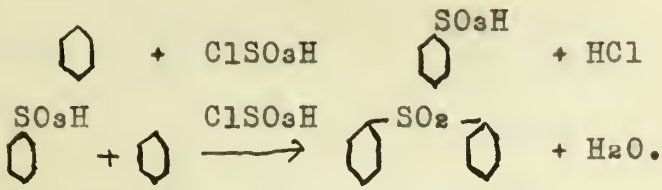
Theoretical Part.

A. Methods of Preparing Sulphones.

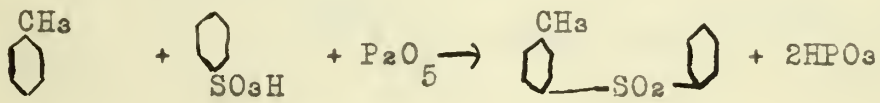
Sulphones are obtained as by-products in the sulphonation of hydrocarbons with fuming sulphuric acid.[6]



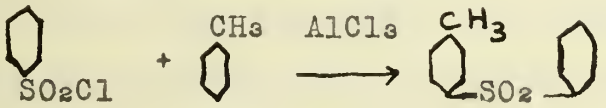
They are obtained as by-products also when the sulphonating agent is chlorosulphonic acid.



However these methods can be used only for those sulphones in which the two radicals are alike. A more general reaction for the preparation of sulphones having different radicles consists in the action of phosphoric anhydride[8] at high temperatures on an aromatic sulphonic acid in the presence of a hydrocarbon.

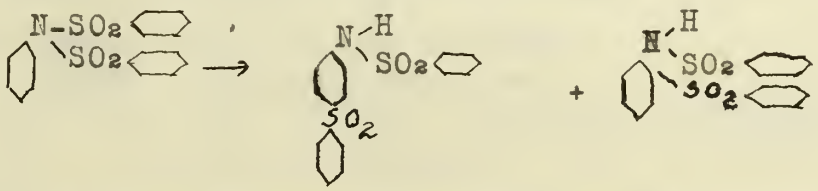


The Friedel and Crafts' reaction[9] has been used extensively in the preparation of these compounds.



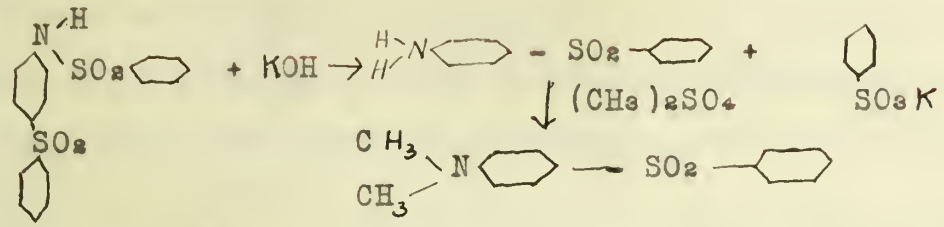
B. Attempted Methods for Preparing P-Dimethylaminodiphenylsulphone.

Chattaway[10] has succeeded in transforming diacylanilides into acylaminoketones and dibenzanilide into benzoyl o- and p- aminobenzophenones. It was thought that it might be possible to rearrange in a similar manner, dibenzenesulphonanilide.



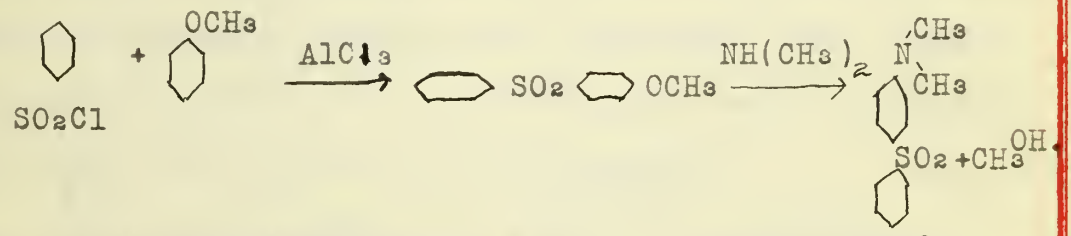
The  SO_2 group bound to the nitrogen was then to be split off by hydrolyzing with potassium hydroxide, and the resulting p-

aminodiphenylsulphone methylated with dimethylsulphate.



The rearrangement was not, however, successful.

P-methoxydiphenylsulphone $\bigcirc SO_2 \bigcirc OCH_3$, has been prepared by M. J. Boeseken.[11] It was thought that this could be heated in a sealed tube with dimethylamine giving the desired compound.



A pure p-methoxydiphenylsulphone was not obtained and for that reason this method of attack was dropped.

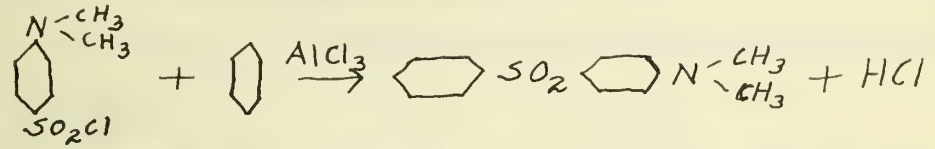
As far as is known amines have not been used in Friedel and Crafts' reactions. As was mentioned above, when dimethylaniline and benzenesulphonyl chloride react without the presence of any other substance, benzenesulphonemethylanilide is formed, instead of p-dimethylaminodiphenylsulphone. It was hoped that the latter compound might be prepared by using aluminum chloride as in the usual Friedel and Crafts' reaction, employing either dimethylaniline itself or carbon bisulphide[11] as the solvent.



Several interesting products were obtained by this method.

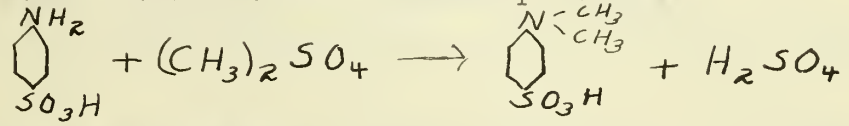
In true Friedel and Crafts' reactions one of the reacting

substances is usually a hydrocarbon. In making diphenylsulphone, benzene and benzenesulphonyl chloride are the reacting substances. It ought to be possible to make p-dimethylaminodiphenylsulphone by using benzene and dimethylsulphanilic acid or the chloride of the acid.



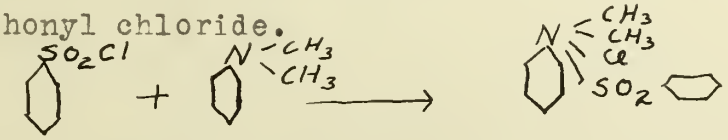
Lack of time prevented the completion of this experiment.

Dimethylsulphate has been used extensively as a methylating agent during the last twenty years. Aniline[12] has been methylated by this reagent giving methylaniline and dimethylaniline. Sulphanilic acid was methylated in a similar manner, and dimethylsulphanilic acid was obtained as one of the products.

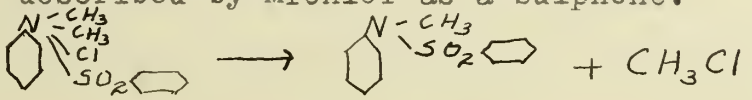


C. Probable explanation of the mechanism of the reaction between dimethylaniline and benzenesulphonylchloride.

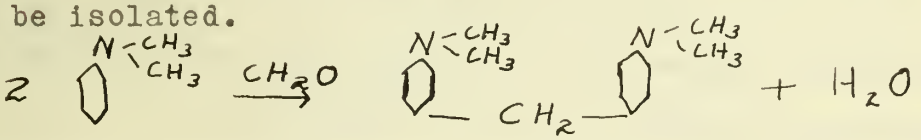
Viewed in the light that has been thrown on the reaction between dimethylaniline and benzenesulphonyl chloride, the probable course of the reaction may be summarized as follows: there is first formed an addition product[13] between the dimethylaniline and the benzenesulphonyl chloride.



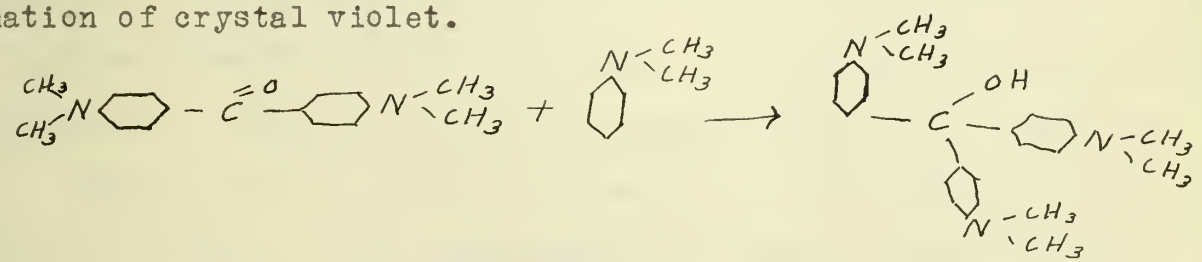
This addition product then loses methylchloride, the resulting product being the benzenesulphonyl derivative of monomethylaniline, the product described by Michler as a sulphone.



A portion of the methyl chloride is, however oxidized. The oxidized methyl chloride behaves exactly as would be the case with formaldehyde, the resulting pp' tetramethyldiaminodiphenylmethane[3] may actually be isolated.



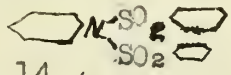
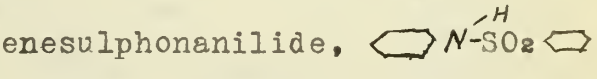
The resulting product is further oxidized to a ketone, and the condensation of the latter with more dimethylaniline results in the formation of crystal violet.



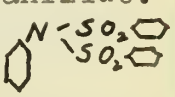
The only product not isolated is the pp' titramethyldiaminobenzophenone, and the difficulty in isolating it is probably due to its great activity.

EXPERIMENTAL PART

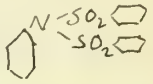
A. Preparation of benzenesulphonanilide and dibenzenesulphonanilide.

To 50 grams of benzenesulphonylchloride 26.3 grams of aniline were added with some water. Sodium hydroxide was added little by little until the solution was alkaline. The whole was shaken vigorously and after the reaction had ceased, a precipitate was filtered off. To the clear filtrate 25 grams of benzenesulphonyl chloride were added gradually, with shaking and sodium hydroxide was added when necessary to keep the solution alkaline. The precipitate was again filtered off, and another 25 gram portion of benzenesulphonyl chloride was added. The solution was filtered again, and the whole precipitate was washed with 50 per cent alcohol. This was then purified by dissolving in hot 95 per cent alcohol and cooling. The compound melted at 142° - 143°, and proved to be dibenzenesulphonanilide, . This melting point agrees with that given by Freundler[14] (143°-144°) and not with that given by Ssolonia[15] (128°-129°). The alkaline filtrate was acidified with hydrochloric acid and benzenesulphonanilide,  was precipitated. This was washed with water and dried. The melting point was 110°-111°. The yield of benzenesulphonanilide was 20 grams and of dibenzenesulphonanilide, 32 grams.

B. Attempted rearrangement of dibenzenesulphonanilide.

One-thirtieth of a mole of dibenzenesulphonanilide  was dissolved in 300 cc. alcohol and 100 cc. concentrated hydrochloric acid and 3 grams of anhydrous zinc chloride were added.

This was refluxed for about 12 hours. The solution was allowed to cool, the precipitate formed was filtered off, washed, and sodium hydroxide solution added to it. The precipitate was washed, and dried and melted at 143.5°. There was no precipitate formed on acidifying the alkaline solution. These facts show that no rearrangement had taken place.

One-thirtieth of a mole of dibenzenesulphonanilide, 
was mixed with 1.5 grams of anhydrous zinc chloride, put into a flask, and heated to about 200° in an oil bath. It was left at about this temperature for a few hours, but the compound had carbonized. This transformation was not attempted again.

C. Preparation of p-meth-oxydiphenylsulphone.

Forty-four and one-tenth grams of benzenesulphonyl chloride were put into a flask with 108.1 grams of anisol; 44.1 grams of aluminum chloride were then added in portions, with shaking. After a few minutes hydrogen chloride was given off and the solution became dark. After reaction had ceased, the solution was steam distilled to remove the excess anisol. Then enough sodium hydroxide was added to dissolve the aluminum hydroxide formed. A very dark precipitate remained which was filtered off and crystallized four times from alcohol. This still had a little color and seemed to be a mixture. Its final melting point was 76°-78°. The melting point as given by Boeseken[11] is 81°.

D. Reactions of demethylaniline and benzenesulphonylchloride.

Forty-four and one-tenth grams of benzenesulphonyl chloride were dissolved in about 50-60 cc. of carbon bisulphide and 33.3 grams

of aluminum chloride were added. The benzenesulphonyl chloride dissolved and formed a dark solution. A small amount of heat was evolved. Then 30.3 grams of dimethylaniline were added slowly. A rather violent reaction took place, hydrogen chloride was given off and a greenish blue precipitate was formed. The solution was steam distilled, and then alkali was added in sufficient amount to dissolve the aluminium hydroxide. The solution was filtered, and the precipitate dissolved in hydrochloric acid. The acid solution was made alkaline and a sticky precipitate was thrown down from which a substance melting at 135°-136° was extracted by means of hot alcohol. Nothing further was done with this.

(b) Eighty-nine grams of dimethylaniline were put into a flask and 45 grams of aluminum chloride were added in small portions. The aluminum chloride reacted with the dimethylaniline and gave a dark green, sometimes, blue liquid and precipitate. A great deal of hydrogen chloride was also given off. 44 grams of benzenesulphonyl chloride were then added in small portions with shaking. On the addition of the benzenesulphonyl chloride, a great deal of heat was evolved, some hydrogen chloride was given off and a dark blue viscous liquid was formed. The shaking was continued until the odor of the benzenesulphonyl chloride was no longer apparent. Water was then added and the solution made sufficiently alkaline to dissolve the aluminum hydroxide. The mixture was steam distilled until all of the excess dimethylaniline had been removed. There was no blue color noticed after the steam distillation. After filtering off a brown precipitate and treating it with concentrated hydrochloric acid, an orange-colored solution was formed. This was fil-

tered and the filtrate diluted with water. A green precipitate was then thrown down, (Product A.). Upon standing and further dilution a little more of it was thrown down. This substance was filtered off, and the filtrate was concentrated and then made alkaline. A brown precipitate was thrown down (Product B.) together with some blue coloring matter. Product A. was crystallized and purified from 95 per cent alcohol. It is a white substance, crystallizing in plates, and melts at 176°-176.5°. It is slightly soluble in ether, and fairly soluble in benzene. It is also soluble in glacial acetic acid but is precipitated upon the addition of water. An analysis for sulphur in this compound was made with the following results:

	Wt. sample	Wt. $BaSO_4$	Per cent S.
I.	.1943 gms.	.1735 gms.	12.26
II.	.1532 "	.1336 "	11.98
III.	.2002 "	.1816 "	12.46
IV.	.2056 "	.1860 "	12.43

An analysis for nitrogen gave the following results.

	Wt. sample	Vol. of Nitrogen	Bar. pressure	Temp.	% Nitrogen
I.	.2654 gms.	17.2 cc	733.3 mn	23°	7.09
II.	.2204 "	14.85 "	745.3 "	31°	7.21

Product B seemed to be a mixture of compounds, since different melting points were observed for the products obtained from different runs. The first time this reaction was run, a melting point of 143°-145° was observed. The second time, the melting point of the product was 170°-173°. The yield of product A was

about 5 grams and of product B about 0.5 grams.

(c) Ninety grams of dimethylaniline were put into a flask and 150 grams of aluminum chloride were added in small portions until most of it dissolved. A dark brown viscous liquid was obtained. Forty-two grams of benzenesulphonyl chloride were added slowly with shaking and a little heating on the water bath. A greenish blue viscous liquid resulted. This was poured into ice water and then steam distilled to drive off the excess dimethylaniline. The solution was filtered, and the residue was treated with concentrated hydrochloric acid. The acid solution was filtered and the filtrate diluted, but this time there was no precipitate formed. However, on making the filtrate alkaline, a blue substance was thrown down. This was recrystallized from alcohol several times but the color, however, never became white. The melting point was 154°-156°. About 1 gram of the substance was obtained.

E. Methylation of sulphanilic acid by means of dimethyl sulphate.

Fifty grams of sulphanilic acid were dissolved in a dilute solution of sodium hydroxide. Ninety grams of dimethyl sulphate were then added in small portions with shaking, always keeping the solution faintly alkaline. After the reaction seemed to be complete, the solution was made faintly acidic with acetic acid and an additional portion of 25 grams of acetic acid was then added. It was found that in order to completely neutralize the sodium a little more than the theoretical amount of acid should be added. The solution was cooled in ice water and after several hours, crystals formed. These were filtered off and crystallized from hot

water containing a little acetic acid. The substance carbonized at about 270°-275°. A solution of its sodium or calcium salt when acidified with hydrochloric acid and treated with a concentrated solution of sodium nitrate according to the method of Michler[6] gave p-nitrodimethylaniline, which was crystallized from alcohol and melted at 162°163°. These facts indicate that the substance was dimethylsulphanilic acid. About 8 grams of it were obtained.

SUMMARY AND CONCLUSIONS.

1. The attempt to rearrange dibenzenesulphonanilide was unsuccessful.

2. In making p-meth—oxydiphenylsulphone, some ortho-compound is probably also formed, thus producing a mixture which is difficult to purify.

3. By using aluminum chloride in the reaction of dimethylaniline and benzenesulphonyl chloride, two compounds were formed, one a slightly basic substance and the other a strongly basic substance. The first compound melts at 176° - 176.5°, and contains 12.35 per cent sulphur and 7.15 per cent nitrogen. It is very soluble in concentrated hydrochloric acid, glacial acetic acid and hot 95 per cent alcohol. It is slightly soluble in ether and benzene. It is insoluble in dilute hydrochloric acid, dilute acetic acid and in alkalies.

The second compound formed may be Michler's ketone in an impure condition.

4. The amount of aluminum chloride used has some effect upon the kind of compounds formed, e.g., with respect to basicity.

5. Dimethylsulphanilic acid can be prepared by the methylation of sulphanilic acid with dimethylsulphate.

6. Sufficient evidence appears now to be available to explain the course of the reaction between dimethylaniline and benzenesulphonyl chloride with the resulting production of crystal violet. The various steps in this reaction have been outlined in the theoretical part of this thesis.

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